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(54) Title: A THERMOPLASTIC FLUORORESIN POROUS BODY, A METHOD FOR THE PRODUCTION THEREOF AND USE OF SAID POROUS BODY FOR PRODUCING A BATTERY CELL					
(57) Abstract					
<p>The present invention relates to a thermoplastic fluororessin porous body which is light in weight and has outstanding characteristics such as mechanical properties, without employing special equipment or a special method, and also a battery cell employing this porous body. The thermoplastic fluororessin porous body is obtained by melt extrusion of a thermoplastic fluororessin in a sheet form or hollow form, after which its degree of crystallization is optionally raised to at least 40 % by heat treatment, following which it is cold drawn, and numerous flattened fine pores produced, by means of which the apparent specific gravity is made no more than 1.7. In the battery cell, the above thermoplastic fluororessin porous body can be carried out for the construction of the separator and/or at least one of the electrodes.</p>					

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SPECIFICATION

A thermoplastic fluororesin porous body, a method for the production thereof and use of said porous body for producing a battery cell

TECHNICAL FIELD

5 The present invention relates to a thermoplastic fluororesin porous body, its method of production and a method of producing a cell. The objectives are to offer a thermoplastic fluororesin porous body with outstanding resistance to chemicals, which is light in weight and excellent in terms of mechanical strength and mass transfer properties, together with a method for the production thereof, and a method for 10 producing a cell employing this porous body.

BACKGROUND ART

As resins of outstanding weatherability and chemical resistance, etc, thermoplastic fluororesins are used for coating materials and for electrical/electronic components, steel pipe linings, chemical plant components and weather-resistant/stain-resistant films, etc. However, fluororesins generally have a high specific 15 gravity and so, in the form of moulded articles, they have the disadvantage of being heavy. On the other hand, attempts have been made to render them porous, and utilise their chemical resistance as separating membranes. Numerous methods and porous bodies derived therefrom have been proposed such as, for example, the 20 method in which polyvinylidene fluoride (hereinafter abbreviated to PVDF) is dissolved in a solvent, then film formation carried out by a wet method, after which the solvent is eliminated and a porous body produced (Japanese Examined Patent Publication No. 59-12691, etc); the method in which inorganic particles are mixed-in, then film production carried out, after which the inorganic particles are eliminated (Japanese 25 Examined Patent Publication No. 62-17614, and Japanese Unexamined Patent Publication Nos 61-242602 and 3-215535, etc); the method of blending an extractable resin and then forming a film after which the resin is extracted (Japanese Examined Patent Publication No. 57-10888, etc); the method of mixing-in an elutable filler, then moulding/ sintering, after which the filler is eluted (Japanese Unexamined Patent 30 Publication No. 51-134761, etc); the method in which a poorly-compatible resin is blended and then film formation conducted, after which drawing is performed and cracks are produced at the interface between the poorly-compatible resin and the matrix resin, and porosity thereby produced (Japanese Examined Patent Publication No. 52-26788, etc); the method of mixing a foaming agent into the PVDF, and then 35 moulding and foaming (Japanese Unexamined Patent Publication Nos 61-53336 and 1-268730, etc); the method of rolling PVDF to less than half its thickness, followed by drawing (Japanese Unexamined Patent Publication No. 58-157831, etc); and the method of irradiating a PVDF film with charged particles in an active gas atmosphere,

and then chemically etching (Japanese Examined Patent Publication No. 60-29742 and Japanese Unexamined Patent Publication No. 3-38228, etc), etc.

However, there are problems with these methods in that, where they are wet film-forming methods they use a considerable amount of solvent, or some other component has to be added and then removed, or etching is performed by some special means. Hence, there is required a facility for recovery of the solvent or additive, or special equipment is needed. Moreover, the performance and properties are lowered by the solvent or additive which remains in the matrix polymer.

Now, in regard to the separators employed in lithium cells of batteries or other such non-aqueous type cells, these have the role of preventing short-circuiting between the positive and negative electrodes, or of ensuring conductivity by retaining electrolyte in the numerous pores introduced in the separator. As typical examples, there are polyethylene (PE) and polypropylene (PP) porous membranes, two-layer membranes formed by affixing PP and PE, and three-layer membranes comprising PE interposed between PP. However, PE and PP are combustible materials and, especially in lithium batteries, a more highly safe material is required.

Further, recently, there have been proposed lithium batteries which use, as the separator, vinylidene fluoride copolymer film which has been swollen by means of a solution formed by dissolving a Li salt such as LiPF₆ in a carbonate solvent (Japanese Unexamined Patent Publication Nos 8-507407 and 8-509100). However, the vinylidene fluoride copolymer film swollen with solvent either has insufficient temperature resistance at high temperatures (50°C and above) or the low temperature (0°C and below) characteristics of the cell, such as capacity, tend to be lowered.

DISCLOSURE OF INVENTION

The present invention has been made as a result of research to overcome the disadvantages of conventional PVDF type porous bodies and cell separators, and to obtain a PVDF porous body which is light and has excellent mechanical strength by a physical method, without employing solvents or additives, and also to obtain a battery separator and a cell employing said porous body.

The present invention is a thermoplastic fluororesin porous body which is characterized in that it comprises a thermoplastic fluororesin containing at least 90 wt% vinylidene fluoride as resin structural units, and has flattened pores of width (minor axis) 0.1 to 3 µm and length (major axis) 0.5 to 20 µm; a method of producing a thermoplastic fluororesin porous body which is characterized in that polyvinylidene fluoride is melt extruded in a sheet form or hollow form, after which, having optionally raised the degree of crystallization to at least 40% by heat-treatment, it is cold drawn and numerous flattened fine pores produced, by means of which the apparent specific

gravity is made no more than 1.7; a battery separator comprising said porous body, and a method of producing a cell employing same.

In the present invention, "thermoplastic fluororesin" is a thermoplastic fluororesin containing at least 90 wt%, and preferably at least 95 wt%, vinylidene fluoride as resin structural units. Thus, it is not restricted to homopolymer comprising one type of monomer and, providing its properties as a thermoplastic fluororesin are retained, it may be a copolymer containing other component(s) in a range up to 10 wt%. If the percentage copolymerization exceeds 10 wt%, it is difficult to obtain the porous body of the present invention. As examples of copolymerizable components, there are tetrafluoroethylene, trifluoroethylene, trifluorochloro-ethylene, vinyl fluoride, hexafluoropropylene, ethylene, perfluoroalkyl vinyl ether and the like. This thermoplastic fluororesin is obtained by emulsion polymerization, suspension polymerization or other such generally-employed polymerization method, and the MFR value is preferably from 0.1 to 500 g/10 minutes.

For the purposes of modification, a small amount of other polymer can be blended with the thermoplastic fluororesin of the present invention and, moreover, there can be freely included conventionally-known antioxidants, thermal decomposition preventives, UV absorbers, hydrolysis resistance improvers, colouring agents (dyes, pigments), antistatic agents, electrical conductors, crystallization nucleating agents, crystallization promoters, plasticizers, ready-slip agents, lubricants, release agents, flame retarders, flame retarding auxiliaries, reinforcing agents, fillers, adhesion auxiliaries, adhesive agents and the like.

The porous body of the present invention has flattened fine pores of width (minor axis) 0.1 to 3 μm and length (major axis) 0.5 to 20 μm . If the size of the fine pores is too small, then it is difficult to achieve a specific gravity reducing effect while, conversely, if it is too large then the filtering effect and the mechanical strength are impaired. The width is preferably 0.2 to 2 μm and length 0.5 to 15 μm .

The apparent specific gravity of the porous body of the present invention is preferably no more than 1.7. More preferably, it is no more than 1.6 and no less than 1.2. The apparent specific gravity can be lowered further by raising the fine pore size or increasing the number of pores but, not only is this technically difficult, it is also undesirable in terms of the membrane performance and strength.

In terms of shape, the porous body of the present invention is mainly a sheet form or hollow form material. "Sheet form material" here encompasses the range from a thick plate (mm order) to a thin film (μm order). Further, a "hollow form material" means the range from a thick pipe to a fine tube, or a hollow fibre or blown film, etc. Of course, it goes without saying that it also encompasses sheet material produced by cutting blown film.

The porous body of the present invention can be produced by melt extrusion of the thermoplastic fluororesin above its melting point and below its decomposition temperature, then cooling and solidifying, followed by careful cold drawing. Of course, besides extrusion, other methods can also be used such as injection moulding and 5 rotary moulding, etc. The draw ratio will depend on the type of resin (percentage copolymerization) and the extrusion and cooling conditions, and will be a factor of from 1.1 to 6, but less than the draw ratio at break, and preferably from 1.2 to 4. The drawing may be either uniaxial or biaxial (simultaneous or consecutive) but, in the case of multistage drawing, care is needed because there is a tendency for the shape 10 of the fine pores to be determined for the most part by the conditions in the first stage. The porous body of the present invention is not readily obtained by hot drawing.

The porous body of the present invention can be produced still more readily by performing a heat treatment prior to drawing and thereby raising the degree of crystallization to at least 40%. It is further preferred that the structure be fixed by 15 another heat treatment following the cold drawing. The recommended heat treatment temperature is 70 to 155°C, and preferably 100 to 150°C. The heat treatment can be conducted in a free state, or alternatively it may be carried out with the shrinkage being restricted, at a fixed length or while being stretched. However, in the stretched state, the percentage stretch should be no more than 10%, and preferably no more 20 than 5%. In short, it is carried out within a range such that the spherulites generated at the time of solidification of the melt are not destroyed, and preferably these are allowed to grow in the state prior to their breakdown and transition to crystallites.

It is possible to introduce crosslinks into the porous body of the present invention by irradiation with a high energy electron beam (normally from 2 to 40 megarad) or 25 gamma-rays, or by a chemical HF abstraction reaction. In this way, it is possible to enhance the heat resistance and mechanical strength of the porous body.

MODES FOR CARRYING OUT THE INVENTION

Below, the present invention is explained in still more specific terms by means of examples, but the present invention is not restricted to these.

30 Now, the various properties in these examples were measured and evaluated by the following methods.

(1) Melt index (MFR) of the thermoplastic fluororesin

This was measured at 230°C with a 12.5 kg load, according to ASTM D 1238.

The units are g/10 minutes.

35 (2) Apparent specific gravity

The value of the weight of the sample divided by (the sample width x length x thickness) was taken as the specific gravity.

(3) Degree of crystallization

This was the value obtained by dividing the enthalpy of crystal fusion measured using a differential scanning calorimeter (DSC at a heating rate of 10°C per minute) by 104.5 J/g (literature value for 100% crystalline polyvinylidene fluoride), expressed as a percentage.

(4) Tensile strength/elongation

The tensile strength was the value obtained when the breaking strength of a strip-shaped sample of width cut to 15 mm, measured at an extension rate of 50 mm/min based on a gauge length of 50 mm, was divided by the cross-sectional area prior to extension. The tensile elongation refers to the extension at break.

Example 1

Vinylidene fluoride homopolymer of MFR 11 was melted at 240°C using a single screw extruder fitted with a 15 cm wide T-die at the tip, and then extruded as a sheet of thickness about 200 µm onto a cooling drum of surface temperature 20°C. The degree of crystallization of this sheet was 38%. (Hereinafter this is referred to as the base sheet.) This sheet was subjected to uniaxial drawing by a factor of 2.5 between two rolls at room temperature (23°C). The two edges showed slight necking, and a somewhat whitened film of thickness 105 µm was obtained. When this film was observed under a microscope it was found that there were numerous flattened fine pores of width about 0.5 to 1 µm and length about 1 to 10 µm. Further, the apparent specific gravity was 1.6, and the tensile strength and elongation were 130 MPa and 150%. When compared to the properties of the undrawn base sheet, which were respectively 1.78, 60 MPa and 250%, it was clear that as well as the specific gravity being lowered by 10%, the strength was raised by a factor of at least 2 and, furthermore, sufficient elongation was retained.

Example 2

When the base sheet obtained in Example 1 was heat treated at a fixed length for 30 minutes at 130°C, the degree of crystallization became 45%. Film of thickness about 120 µm obtained by drawing this sheet by a factor of 2.1 at room temperature had an apparent specific gravity of 1.58 and a tensile strength and elongation of 140 MPa and 110%. When viewed under a microscope numerous comparatively uniform, flattened, fine pores of width about 1 µm and length 5 - 10 µm were observed.

Comparative Example 1

When the base sheet obtained in Example 1 was hot drawn by a factor of 3 at 120°C, the tensile strength was markedly enhanced, at 190 MPa, but the apparent specific gravity was 1.79 and no fine pores were observed. Even when this hot drawn film was further cold drawn by a factor of 1.3, no pores were noted.

Example 3, Comparative Example 2

5 Polyvinylidene fluoride of MFR 5 in which 4% hexafluoro-propylene was copolymerized (Example 3), and poly-vinylidene fluoride of MFR 7 in which 14% hexafluoro-propylene was copolymerized (Comparative Example 2), were respectively extruded at 230°C or 220°C using the same equipment as in Example 1, and base sheet obtained. Both were cold drawn by a factor of 3.5 but, whereas fine pores of width 0.3 to 3 µm and length 0.8 to 8 µm were observed in the film of Example 3, no fine pores were noted in the film of Comparative Example 2.

Example 4

10 As a negative electrode active material support, there was used a slurry obtained by adding 100 parts by weight of coal pitch coke, which had been pulverized in a ball mill, to a solution of 10 parts by weight of polyvinylidene fluoride (Kynar 500, made by Elf Atochem; MFR at 230°C with a 2.16 kg load = 0.03 g/10 min), as a binder, dissolved in N-methylpyrrolidone, to form a slurry (paste). This slurry was applied onto 15 both faces of copper foil of thickness 20 µm and then left for 1 hour at 120°C, after which it was dried under reduced pressure and pressed, and a negative electrode of thickness 140 µm and width 20 mm obtained.

20 Next, a positive electrode was obtained in the following manner. 100 parts by weight of LiCoO₂, as the positive electrode active material, and 6 parts by weight of graphite, as a conducting agent, were dispersed in N-methylpyrrolidone along with 10 parts by weight of polyvinylidene fluoride as a binder, to form a slurry (paste). This slurry was applied to both faces of aluminium foil of thickness 20 µm and left for 1 hour at 120°C, after which it was dried under reduced pressure and pressed, and a positive electrode of thickness 175 µm and width 20 mm obtained.

25 Using the negative and positive electrodes thus obtained, and using porous film of thickness 30 µm prepared by the same method as in Example 1 as a separator, these were laminated in the order separator/negative electrode /separator/positive electrode/separator, after which the laminate was wound in a coil shape, and a coil-shaped electrode body obtained. Next, lead wires were attached to 30 the respective electrodes of this electrode body, after which it was fitted in a stainless steel holder. Into this was injected, as electrolyte, a solution obtained by dissolving 1M of LiPF₆ in an equi-volume mixture of propylene carbonate and 1,2-dimethoxyethane.

35 A charging/discharging test was carried out by initially charging up to 4.1 V at a current density of 30 mA per 1g of carbon and then discharging down to 2.5 V at the same current density. The second time, and thereafter, charging and discharging were again repeated under the same conditions and the cell evaluated according to the discharge capacity. As a result, the discharge capacity on the 100th cycle was good, being over 60% that on the 10th cycle.

INDUSTRIAL APPLICABILITY

As well as for various types of shaped articles, the porous body of the present invention is useful as a filter or other such filtration material, and as a separation membrane such as separator for a battery, etc. Moreover, it can serve as a base 5 material for membranes with added functionality, by supporting ion-exchange groups or adsorbent materials.

In particular, when applied to lithium cells/batteries, the porous body of the present invention (normally in the form of film) can be used as a separator or as an 10 electrode by complexing with an electrode active material. In the case of a separator, the porous film is impregnated with an electrolyte solution formed by dissolving at least one type of lithium salt selected from LiPF₆, LiBF₄, LiClO₄, LiAsF₆, LiN(CF₃SO₂)₂, LiCF₃SO₃, LiSbF₆ and the like, in a suitable solvent (chiefly a carbonate such as ethylene carbonate, propylene carbonate or dimethyl carbonate, etc). Further, the 15 porous body can be used as a support for a gel electrolyte (polymer gel swollen with a solution containing electrolyte).

Further, the porous body of the present invention can be used as a separator or electrode support in nickel/ hydrogen batteries, silver/zinc batteries, lead/acid batteries, zinc/air batteries, nickel/cadmium batteries, alkali batteries or zinc bromide batteries, etc.

20 As explained above, the porous body of the present invention is light in weight and outstanding in its mechanical characteristics, and it is valuable for various kinds of filtration materials and for separating membranes, etc. Furthermore, when employed as the separator in a lithium cell, etc, since the PVDF is poorly combustible, it forms a battery which is safer than in the case where a polyethylene separator is used.

CLAIMS

1 A thermoplastic fluororesin porous body characterized in that it comprises a thermoplastic fluororesin containing at least 90 wt% vinylidene fluoride as resin structural units, and it has flattened pores of width (minor axis) 0.1 to 3 μm and length (major axis) 0.5 to 20 μm .

5 2 A thermoplastic fluororesin porous body according to Claim 1 characterized in that the porous body is a sheet-form material or hollow-form material.

10 3 A method of producing a thermoplastic fluororesin porous body according to Claim 1 or 2 characterized in that the thermoplastic fluororesin is melt extruded in a sheet or hollow form, after which it is cold drawn, and numerous flattened fine pores produced and crosslinking effected by radiation or chemical treatment.

15 4 A method of producing a thermoplastic fluororesin porous body according to Claim 1 or 2 characterized in that the thermoplastic fluororesin is melt extruded in a sheet form or hollow form, after which it is heat-treated and the degree of crystallization made at least 40%, following which it is cold drawn, and numerous flattened fine pores produced and then by a further heat treatment these fine pores are fixed.

20 5 A battery cell comprising an anode, a cathode and a separator, characterized in that the separator and/or at least one electrode are constructed from a thermoplastic fluororesin porous body, and this thermoplastic fluororesin porous body as defined in Claim 1 or 2.

25 6 A method of producing a cell according to Claim 5 characterized in that the thermoplastic fluororesin porous body is obtained by melt extruding polyvinylidene fluoride in a sheet form, after which it is cold drawn, and numerous flattened fine pores are produced, by means of which the apparent specific gravity is made no more than 1.7.

7 A method of producing a cell according to Claim 5 characterized in that the thermoplastic fluororesin porous body is crosslinked by radiation or chemical treatment.

30 8 A battery separator comprising a thermoplastic fluororesin sheet characterized in that it comprises a thermoplastic fluororesin porous body according to Claim 1 or 2.

35 9 A method for producing the battery separator of Claim 8 characterized in that the thermoplastic fluororesin is melt extruded in sheet form, after which it is cold drawn, and numerous flattened fine pores are produced and possibly crosslinking of the-said fluororesin is carried out by radiation or chemical treatment.

10 Use of a thermoplastic fluororesin porous body as a filter or filtration material, such as a separation membrane by supporting ion-exchange groups or adsorbent materials.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 97/04885

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B29C55/00 B01D67/00 H01M2/00 //B29K27:12

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B29C B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 553 050 A (KUREHA CHEMICAL IND CO LTD) 19 September 1979 see page 2, line 9 - line 32; example 10 ---	1-10
X	DATABASE WPI Section Ch, Week 8408 Derwent Publications Ltd., London, GB; Class A14, AN 84-045627 XP002049956 & JP 59 006 231 A (MITSUBISHI RAYON CO LTD), 13 January 1984 see abstract -- -/-	1,2,5,8, 10

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Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 8712 Derwent Publications Ltd., London, GB; Class A18, AN 87-083176 XP002049957 & JP 62 033 878 A (MITSUBISHI RAYON CO LTD) , 13 February 1987 see abstract ----	3
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